Rotationally Resolved Photoelectron Study of O_2: Identification of the Vibrational Progressions for $O_2^+(2^2\Pi_u, {}^2\Sigma_u^-)$ at 19.6-21.0 eV

C.-W. Hsu[1], M. Evans[2], S. Stimson[2], and C. Y. Ng[2]
[1]Chemical Science Division, Lawrence Berkeley National Laboratory Berkeley, CA 94720, USA
[2]Ames Laboratory, USDOE and Department of Chemistry, Iowa State University Ames, IA 50011, USA

INTRODUCTION

In this abstract, we present the results of a rotationally resolved pulsed field ionization photoelectron (PFI-PE) study of the vibrational bands observed at 19.63 and 20.35 eV. These bands have been firmly established by experiments previously (e.g. [1,2]), but definitive assignment of these progressions remains to be made. The rotational structures observed for these bands make possible the unambiguous assignment of the progressions beginning at 19.63 and 20.35 eV to transitions associated with the $O_2^+(2^2\Pi_u)$ and $O_2^+({}^2\Sigma_u^-)$ states, respectively.

EXPERIMENT

The experimental arrangement has been described in detail previously [3]. The O_2 sample was introduced as an effusive O_2 beam ($\approx 10^{-3}$ Torr in the photoionization/photoexcitation region) through a metal orifice (diameter = 0.5 mm) at room temperature and a distance of 0.5 cm from the photoionization/photoexcitation region. The rotational temperature of the O_2 sample is expected to be ≈298 K. This, together with other improvements of the electron lenses and magnetic shielding of the hemispherical energy analyzer, has made possible a nearly 100 fold increase in the PFI-PE intensity as compared to that observed previously using a neat O_2 supersonic beam [3]. The PFI-PE resolution achieved is 0.6 meV or 5 cm^{-1} (FWHM) as measured by the PFI-PE band for $Ne^+({}^2P_{3/2})$.

RESULTS

Figure 1 depicts the PFI-PE spectrum for O_2 (upper curve) in the region of 19.590-19.650 eV, which corresponds to the first vibrational bands observed initially by Merkt and Guyon [2]. The relative intensities for rotational transitions resolved here were simulated using the Buckingham-Orr-Sichel (BOS) model [4]. This model was derived to predict rotational line strengths observed in one photon ionization of diatomic molecules.

A successful simulation of the experimental PFI-PE band at 19.63 eV is obtained assuming $O_2^+({}^2\Pi_u, v^+, N^+) \leftarrow O_2(X^3\Sigma_g^-, v \leq 0, N'')$ ionization transitions. The angular momentum coupling constants were calculated using the formula for a Hund's case (b) to (a) transition. The known spectroscopic constants for the $O_2(X^3\Sigma_g^-)$ state were used [5]. Due to the nuclear spin statistics, the even N'' rotational levels in $O_2(X^3\Pi_g)$ do not exist. The spin-rotation splittings for $O_2(X^3\Sigma_g^-)$ are in the range of 0.1-0.2 meV for each

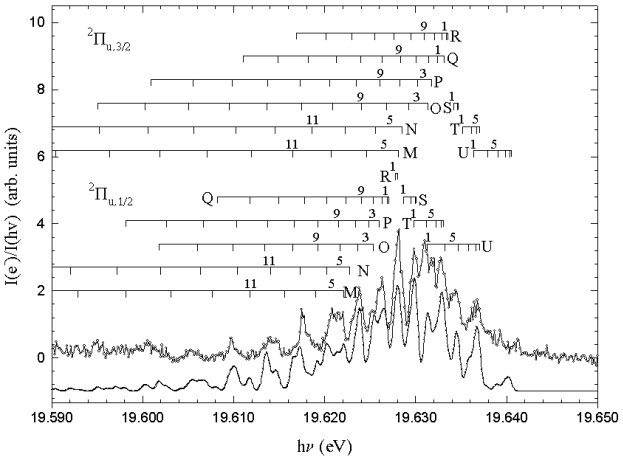

Figure 1. Comparison of the simulated (lower curve, solid circles) and experimental (upper curve, open circles) PFI-PE spectrum of O_2 in the energy range of 19.590–19.650 eV obtained using a neat effusive O_2 beam at 298 K.

rotational state and result in a broadening of the rotational lines by ≈0.1 meV in the simulated spectra. The best fit to the experimental spectrum (lower curve of Fig. 1) was obtained using C_λ = 0.25 (The BOS coefficients) for λ=1-4 for both the spin-orbit components and a temperature of 300 K for O_2. The rotational branches ΔN (= N^+-N'') = -4, -3, -2, -1, 0, 1, 2, 3, and 4, which are designated correspondingly as the M, N, O P, Q, R, S, T, and U branches, are marked in Fig. 1. For a g ↔ u transition, the photoelectron angular momentum *l* must be even. Thus, the partial waves for the ejected electron are restricted to *l* = 0, 2, and 4.

The simulation of the PFI-PE band shown in Fig. 1 yields IE[$O_2^+(2^2\Pi_{u1/2})$] = 19.62684±0.00050 eV and IE[$O_2^+(2^2\Pi_{u3/2})$] = 19.63287±0.00050 eV. Considering the fact that the origin of 19.6299±0.0005 eV found is consistent with the predicted IE[$O_2^+(2^2\Pi_u)$] of 19.69 eV, we conclude that the weak PFI-PE vibrational band at 19.63 eV is the origin, i.e., the v^+ = 0 level, of the vibrational progression. We note that the observed ω_e values [2] of 0.110-0.100 eV for this progression are also in accord with the theoretical ω_e of 0.106 eV [1]. The spin-orbit splitting and rotational constant (B_0) for the $O_2^+(2^2\Pi_u, v^+=0)$ level are determined to be 54±3 and 1.08±0.02 cm^{-1}, respectively. Using the latter value, we calculated a value of 1.397±0.012 Å for the equilibrium bond distance (r_e) of $O_2^+(2^2\Pi_u)$, which agrees well with the theoretical r_e of 1.403 Å. We note that the $O_2^+(2^2\Pi_u)$ state correlates to the third dissociation limit [$O(^3P)$ + $O^+(^2D)$] at 22.06 eV[2], and thus has a bond dissociation energy of 2.43 eV [1].

The rotationally resolved PFI-PE spectrum for O_2 (upper curve) in the energy region of 20.320–20.365 eV is plotted in Fig. 2. Based on the $^{18}O_2$ TPE study of Merkt and Guyon[2], we assume that this band is the origin, i.e., the v^+=0 level, of the vibrational progression. The rotational structure of this band indicates that it is associated with an excited O_2^+ state of the Σ symmetry. Since the PFI-PE resolution is not sufficient for resolving the spin-rotation splittings, the PFI-PE spectrum of Fig. 2 cannot distinguish between the $^4\Sigma$ and $^2\Sigma$ states. However, on the basis of the fitting and photoionization selection rules [6], we can exclude the $^{2,4}\Sigma_g^-$, $^{2,4}\Sigma_u^+$, and $^{2,4}\Sigma_g^+$ states are possible candidates. Considering the IE and ω_e values for excited O_2^+ states predicted by Beebe *et al.* in the energy region of 19.5-21.5 eV [7], the most likely candidate is the $O_2^+(^2\Sigma_u^-)$ state. Although the predicted ω_e (825 cm^{-1}) [7] value for this state is close to the experimental [1,2] value of 810 cm^{-1}, the predicted IE (≈21.2 eV) [7] for this state is more than 0.8 eV greater than the experimental IE of 20.35 eV. Assuming that the ionization transitions correspond to $O_2^+(^2\Sigma_u^-, v^+=0, N^+) \leftarrow O_2(X^3\Sigma_g^-, v''=0, N'')$ and that the rotational temperature of O_2 is 300 K, we obtained an excellent fit (lower curve of Fig. 2) to the experimental spectrum. The angular momentum coupling constants were calculated using the formula for a Hund's case (b) to (b) transition. The

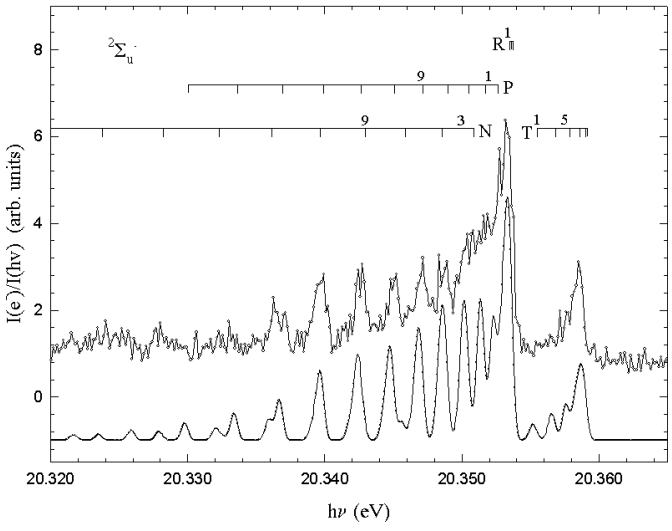

Figure 2. Comparison of the simulated (lower curve, solid circles) and experimental (upper curve, open circles) PFI-PE spectrum of O_2 in the energy range of 20.320–20.365 eV obtained using an effusive O_2 beam at 298 K.

simulation yields an IE value of 20.3526±0.0005 eV and a B_0 value of 1.14±0.02 cm^{-1}. The latter value corresponds to r_e = 1.360±0.012 Å, which is larger than r_e =1.30 Å for the $O_2^+(B^2\Sigma_g^-)$ state, but significantly smaller than the theoretical prediction [7] of r_e=1.522 Å for the $O_2^+(^2\Sigma_u^-)$ state. Both experiment [1,2] and theory [1,7] show that the $O_2^+(B^2\Sigma_g^-)$ and $O_2^+(^2\Sigma_u^-)$ states correlate to the dissociation limit of $O(^3P) + O^+(^2D)$. Thus, the dissociation energy for $O_2^+(^2\Sigma_u^-)$ determined here is 1.707 eV. The BOS coefficients obtained from the stimulation are C_1=0.7 and C_3=0.3, indicating that the *l* values for the out going electron are restricted to 0, 2, and 4. The rotational transitions for the N, P, R and T branches are marked in Fig. 2.

CONCLUSION

In summary, we have demonstrated that rotationally resolved photoelectron spectroscopy, together with high level theoretical *ab initio* calculations, can provide unambiguous assignments of weak photoelectron bands observed in the inner-valence region.

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Principal investigator: Cheuk-Yiu Ng, Ames Laboratory, USDOE and Department of Chemistry, Iowa State University. Email: cyng@ameslab.gov. Telephone: 515-294-4225.